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Influence of fuel properties and composition on NO_x emissions from biodiesel powered diesel engines: A review

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ABSTRACT

Biodiesel has proved to be an environment friendly alternative fuel for diesel engine because it can alleviate regulated and unregulated exhaust emissions. However, most researchers have observed a significant increase in NO_x emissions with biodiesel when compared to petrodiesel. The exact cause of this increase is still unclear; however, researchers believe that the fuel properties have been shown to effect the emissions of NO_x. The present work reviews the effect of fuel properties and composition on NO_x emissions from biodiesel fuelled engines. The paper is organised in three sections. The first section deals with the NO_x formation mechanisms. In the following section, the reasons for increased NO_x emissions of biodiesel fuel are discussed. After this, the influence of composition and fuel properties on NO_x emissions from biodiesel fuelled engines has been reviewed. Finally, some general conclusions concerning this problem are summarised and further researches are pointed out.

Contents

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1. Introduction

The most important aspect of air quality management is to control the harmful emissions from internal combustion engines. In order to improve the air quality, stringent emission norms were introduced worldwide. The limit values were lowered many times over the last decades and will be set to further lower values for the coming years. Burning biodiesel in diesel engine produces a significant reduction in emissions of particulate matter, HC and CO but in most cases also causes an increase in NO_x emissions (about 10–23%) when compared to diesel fuel [1–4]. This increase in NO_x emissions is termed as biodiesel NO_x effect. It has been a long-standing issue and yet to be satisfactorily resolved. The US Environmental Protection Agency (EPA) enlisted NO_x as one of the criteria pollutants that can affect the respiratory system. The biodiesel market in the U.S alone is expected to reach 4000 million gallons in 2030 [5]. As the use of biodiesel has increased enormously, the rise in NO_x emissions could become a significant barrier to market expansion. Van Gerpen et al. [6] suggested that the reason for the higher NO_x emissions is mainly due to changes in the chemical composition and the physical properties of the fuel. Therefore it is necessary to understand the effect of fuel properties on biodiesel NO_x emissions and to develop improved techniques for NO_x abatement. The objective of this paper is to provide a complete literature review on the influence of fuel composition and properties on the NO_x emissions when fuelling with biodiesel.

2. NO_x formation mechanisms

NO_x is a mixture of gases which consists of nitric oxide (NO), dinitrogen dioxide (N_2O_2), nitrous oxide (N_2O), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). In most high-temperature combustion processes, the majority (95%) of NO_x produced is in the form of nitric oxide (NO) [7]. Understanding NO production in diesel engine combustion requires a comprehensive analysis of NO_x formation mechanisms. This section deals with the oxides of nitrogen formation pathways such as thermal, prompt, and N_2O mechanisms. Generally, biodiesel does not contain fuel-bound nitrogen, so NO formation by the fuel NO mechanism can be considered negligible [8].

2.1. Thermal NO

Thermal NO formation mechanism is the dominant source of NO_x in combustion system. It is formed by the reaction of atmospheric nitrogen with oxygen due to combustion at elevated temperatures (above1800 K). The three reactions producing thermal NO proposed by Zeldovich [9] are:

$$N_2 + O \leftrightarrow NO + N \tag{1}$$

$$N + O_2 \leftrightarrow NO + O \tag{2}$$

$$N + OH \leftrightarrow NO + H \tag{3}$$

Due to high activation energy requirement of Reaction (1), NO production by thermal mechanism proceeds at a slower rate than the oxidation of hydrocarbons. The NO formation rate can be approximated by:

$$[NO] = k\,e^{-K/T}[N_2][O_2]^{1/2}t \tag{4}$$

where k and K are reaction constants, T is absolute temperature, and t is time [10]. Eq. (4) indicates that thermal NO formation is an exponential function of temperature. The other factors that influence thermal NO formation rate are oxygen, nitrogen concentrations and residence time of reaction products.

2.2. Prompt NO

Prompt NO is generally an important mechanism in low temperature, fuel-rich combustion processes where residence times are short. According to prompt or Fenimore mechanism [11], formation of free radicals in the flame front of hydrocarbon flames leads to rapid production of NO. Generally, the prompt NO contribution to total NO from combustion process is considered less important when compared to thermal NO. However, in biodiesel combustion, significant quantities of NO are formed by prompt mechanism [12].

$$CH + N_2 \leftrightarrow HCN + N \tag{5}$$

$$C_2 + N_2 \leftrightarrow 2CN \tag{6}$$

$$CN + O_2 \leftrightarrow NO + CO \tag{7}$$

The rate of HCN and NO formation increases with the concentration of hydrocarbon radicals. Fenimore suggested that the N-atom produced from Reaction (5) could form NO through Reaction (3). The cyanogen produced in Reaction (6) would react with diatomic oxygen or with oxygen atom to form nitric oxide. Such reactions require relatively low activation energy and the rate of NO formation is very rapid which is comparable to that of the oxidation of fuel. This means that NO formation can takes place even at much lower temperatures (below 750 °C).

2.3. N_2O pathway

In this mechanism, the atomic oxygen reacts with N_2 to form N_2O by a three body reaction.

$$O + N_2 + M \leftrightarrow N_2O + M \tag{8}$$

where M is a molecule that is required to complete this reaction. The N_2O formed in Reaction (8) can then react to form NO.

$$N_2O + O \leftrightarrow NO + NO \tag{9}$$

This mechanism is important in combustion process under elevated pressure and lean air fuel ratio conditions [13].

3. Causes of biodiesel NO_x effect

There are many factors that have an impact on NO_x formation from diesel engine. NO_x formation is primarily a function of pressure, reaction temperature, residence time of combustion products, premixed portion of combustion, availability of excess oxygen, ignition delay period, heat removal rate and the operational parameters of the engine [14]. An overwhelming number of studies have shown that high isentropic bulk modulus of biodiesel causes an artificial advance in injection timing relative to petrodiesel, and higher NO_x emissions [15–18]. In pump-line-nozzle (PLN) injection system, earlier injection timing causes an increase in the fuel mass delivery and residence time, which results in very high reaction temperature and more NO_x formation. McCormick et al. [19] did not find any increase in NO_x emissions with common rail injection system equipped engines. However, Zhang and Boehman [20] found much higher NO_x emissions with common rail system, and concluded that injection timing shift alone could not be the reason for biodiesel NO_x effect.

Benajes et al. [21] show significant effects of adiabatic flame temperature, heat release rate and stoichiometric burning on NO_x formation in diesel engines. The adiabatic flame temperature of biodiesel is reported to have slightly higher than petrodiesel due to complete combustion resulting from fuel bound oxygen [22]. In contrast, Monyem et al. [16] have shown that biodiesel has lower adiabatic flame temperature than petrodiesel. Some studies [23–25] report the higher heat release rate of biodiesel as a

possible cause for the biodiesel NO_x effect. Szybist et al. [18], however, observe a lower rate of heat release for biodiesel fuel at all loads. This conclusion is further supported by extensive experimental work by Bittle et al. [26]. Mueller et al. [27] observed increased stoichiometric burning of biodiesel combustion which could lead to rise in temperature and NO_x. Many researchers [28–30] reported the radiative heat transfer from in-cylinder soot can significantly influence NO_x formation rate. The oxygen content in biodiesel could cause reduced soot formation [31], which results in lessened radiative heat transfer and thus increase of temperature [32]. On the contrary, Agarwal et al. [33] observed increased formation of particulate matter with biodiesel fuel than diesel fuel.

A change in biodiesel fuel properties might lead to increased ignition delay period. Generally, longer ignition delay increases the premixed burn fraction which is responsible for increased NO_x generation [34]. Choi and Reitz [35] reported that fuel mass delivery rates and spray tip penetrations increase when biodiesel is used as a diesel engine fuel. Yuan and Hansen [36] conducted computational study using Zeldovich NO_x formation model together with a Kelvine–Helmholtz–Rayleighe–Taylor (KH–RT) spray breakup model and concluded that decreased spray cone angle and advanced start of injection of biodiesel influences NO_x formation. Biodiesel requires longer pulse-width than diesel in electronic controlled engines due to its low calorific value causing more quantity of fuel entry into the cylinder which results in high temperature and NO_x [37]. The higher boiling point, viscosity, and surface tension of biodiesel fuel may contribute to the increased NO_x emissions [38]. Yuan et al. [39] have claimed that biodiesel has more widespread high-temperature distribution areas than diesel that could contribute higher NO_x. Varuvel et al. [40] concluded that the increased premixed combustion of biodiesel fuel is one of the reasons for biodiesel NO_x effect.

CH and OH radicals are continuously formed during combustion reactions. The formation of CH-radicals is an indicator of low temperature pre-combustion reactions, which is the first step for the combustion process, once fuel is evaporated. OH radicals are formed during high temperature reactions and are located in the flame front, where vapourized fuel reaches the highest temperatures [41]. Brezinsky et al. [42] claimed that the high rate of acetylene production from the unsaturated fatty acids of biodiesel is the major cause of increased NO_x formation. The acetylene is, responsible for hydrocarbon CH radical generation and prompt NO_x. Recently, Violi et al. [43] conducted an experiment to analyse biodiesel combustion using shock tube and detected reduced formation of OH radicals. Moreover, they observed decreased reactivity of biodiesel over a certain low to intermediate temperature range (Negative temperature coefficient (NTC) behaviour) [44]. The increased rate of CH radical formation, lower rate of OH radical generation and NTC behaviour of biodiesel, indicates that biodiesel combustion is a low temperature reaction when compared to mineral diesel combustion. Therefore factors such as elevated adiabatic flame temperature, higher heat release rate and stoichiometric burning might not be the major reasons for biodiesel NO_x effect. The US National Renewable Energy Laboratory (NREL) also reported the increased formation of prompt NO_x as the main reason for biodiesel NO_x effect and they suggested the use of antioxidants as a prompt NO_x control strategy [12]. Based on their suggestion we have conducted emission tests on Jatropha biodiesel fuelled diesel DI diesel engine with antioxidant additives and observed significant reductions in NO_x [45]. This reduction is possibly due to the suppression of free radical formation by antioxidants. The biodiesel NO_x effect has been reviewed in detail by Jacobs et al. [46] and Hoekman and Robbins [47]. The NO_x mitigation techniques applicable to biodiesel fuels are reviewed by Rajasekar et al. [48].

4. Effect of fuel properties on biodiesel NO_x emissions

There is widespread agreement that no single factor is responsible for biodiesel NO_x effect. The physical and chemical properties of biodiesel may influence combustion temperature, residence time and injection pattern and thus NO_x emissions. The fuel properties such as bulk modulus, fuel bound oxygen, degree of saturation, cetane number, viscosity, density, surface tension, thermal conductivity, heat capacity, vapour diffusion coefficient all have significant impact on the engine performance and emissions. The physical and chemical properties of common biodiesel fuels and their NO_x emissions rate are presented Table 1.

Haseeb et al. [49] compared the NO_x emissions of different biodiesel fuels with diesel fuel.

4.1. Effect of bulk modulus of compressibility

The isentropic (dynamic) secant bulk modulus, a preferred injection system parameter is a measure of resistance to compressibility. It decreases with temperature, increases with pressure but also influenced by velocity of sound and density of fuel. Vegetable oils and their methyl esters are less compressible than diesel, so that the pressure wave from the fuel pump is rapidly transferred to the injector nozzle which will cause the needle to open earlier [6]. The early opening of needle leads to increased mass delivery and elevated temperature and thus more NO_x. Tat and Van Gerpen [66] studied the effect of fuel property changes on injection timing and concluded that the high value of bulk modulus and speed of sound could cause approximately 1° of injection timing advance and this effect may be partially responsible for the increase in NO_x. They reported that the densities, speed of sound and isentropic bulk modulus are higher for the more unsaturated esters and the increase in properties is not uniform as each double bond is added. Moreover, they found that the speed of sound and isentropic bulk modulus increase as the chain length increases.

Kegl [67] studied the influence of fuel on inline fuel injection system at different operating regimes by numerical simulation. She compared all the injection parameters of B100, B75, B50 and B25 with diesel and found that the injection delay reduces with B100 and other blends because of higher values of bulk modulus. Furthermore, she observed that mean injection pressure and mean injection rate increases with higher content of biodiesel in blends. Gumusa et al. [68] report similar results. Szybist et al. [18] examined emissions from biodiesel and Fischer–Tropsch diesel (low bulk modulus bio-fuel) and they observed lowest NO_x emissions with Fischer–Tropsch diesel. Recently, Caresana [69] studied the impact of biodiesel bulk modulus on injection pressure and injection timing and concluded that advance in injection timing due to high bulk modulus of biodiesel is less high than commonly believed. The bulk modulus, density and velocity of sound values of some biodiesel fuels are presented in Table 2. It is shown in Table 2 that the methyl soy ester has highest values of bulk modulus of compressibility and velocity of sound and also produces more NO_x (Table 1).

The bulk modulus effect on NO_x emissions can be reduced by retarding the injection timing and by preheating the fuel. Monyem et al. [16] have shown a 35% reduction in NO_x emissions for a 6° retardation in injection and Ren and Li [71] found a significant reduction with preheated biodiesel. However, the ignition timing retardation also leads to an increase in soot or PM emissions and hence would require recertification of the engine for emissions standard compliance. Modern engines are equipped with common rail injection systems and the fuel mass delivery can be precisely controlled by electronic sensors. However, such types of engines also produce more NO_x emissions when fuelled with biodiesel [72].

Table 1
Physical and chemical properties of various methyl esters of fatty acids.

Fatty acid methyl ester	Degree of saturation (% by wt.)	Relative change in NO_x (%)	Iodine value	Cetane number	Kinematic viscosity at 40 °C (mm^2/s)
Soybean	15.22	+ 13.1 [50]	117–143	46.2	4.08
Rapeseed	4.34	+ 8.3 [51]	94–120	54.4	6.7
Yellow grease	36.51	+11.6 [50]	80–100	62.6	5.92
Sunflower	9.34	+11 [52]	110–143	46.6	4.22
Canola	7	+6 [53]	110–120	51.6	4.02
Cottonseed	23.8	+10 [54]	90–119	51.2	6.1
Jatropha	26.2	+12.97 [55]	95–105	52.31	4.8
Tall oil	4	+25 [56]	125–135	50	5.3
Rice bran	14.2–21.1	+2.7 [57]	99–108	51	4.958
Linseed	7.9	+13 [58]	168–204	55	3.752
Lard	41–50	+2.5 [59]	62.5	63.6	4.8
Palm	45.6	−5 [60]	44–58	56.2	4.958
Coconut	81.5	−20 [61]	8–10	68	2.726
Beef tallow	47–63	0 [8]	53.6	58.8	4.824
Mahua	46.2	+11.6 [62]	88	51	3.98
Neem	39.6	−4.5 [63]	65–80	50.4	5.213
Olive	20.2	+30 [64]	75–94	57	4.5
Pongamia pinnata	29.2	−20 [65]	117	51	4.93

Therefore, bulk modulus of biodiesel has minor effect on NO_x emissions [47].

4.2. Effect of fuel composition

Biodiesel consists of fatty acids produced by the transesterification of vegetable oils. In the resulting transesterification process the glycerol molecule of fatty acid is replaced with three alcohol molecules. Fatty acids are long chain organic acids having usually 4–30 carbon atoms, which is either saturated or unsaturated. Their composition determines the physical properties, calorific value and stability of biodiesel. Saturated fatty acids have no carbon–carbon double bonds and unsaturated fatty acids have one or more double bonds. A fatty acid with one double bond is called monounsaturated and fatty acid with two or more double bonds is termed polyunsaturated fatty acids (PUFA). Each fatty acid differs from others in lengths of the carbon chain and the number of carbon–carbon double bonds. The fatty acids are denoted by XX:Y, where XX designates the number of carbon atoms in the fatty acid chain and Y the number of double bonds. The most common fatty esters contained in biodiesel are mainly of C16 and C18 fatty acids including palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) [73]. Palmitic acid and stearic acids are saturated fatty acids, and others are unsaturated fatty acids. Fuel compositions of various feedstocks are analysed by Singh and Dipti [74]. Feedstocks, such as chicken fat, palm oil and coconut oil contain higher percentage of saturated fatty acids whereas, soybean oil, canola oil, sunflower oil and corn oil has higher percentage of unsaturated fatty acids.

McCormick et al. [75] found that the molecular structure of biodiesel can have a direct impact on NO_x emissions. They investigated the relationship between NO_x emissions and Iodine value and revealed that NO_x increases with iodine value of biodiesel. Iodine number (IV) is a measure of degree of unsaturation of the fatty acid; a high iodine number indicates a high degree of unsaturation. Wyatt et al. [76] conducted emission tests with the tallow methyl ester (IV 53.6), lard methyl ester (IV 62.5) and chicken fat esters (IV 77.4) and compared with soybean oil biodiesel (IV 129.1) and observed that NO_x emissions are linearly correlated with iodine value of fatty acid ester. Moreover, Peterson et al. [77] performed emission tests on coconut ethyl ester, used hydrogenated soy methyl ester, rapeseed ethyl ester, mustard ethyl ester, safflower ethyl ester, and a commercial methyl ester of soy oil and reported that as the iodine number increased from 7.88 to 129.5, the NO_x emissions were increased by 29.3%. Table 1 also indicate that the lowest iodine value fuels such as coconut and palm oil methyl esters have shown least NO_x emissions.

Most of the commercial biodiesel feedstocks are made from unsaturated fatty acids which may lead to higher NO_x emissions when compared to petrodiesel. Knothe et al. [78] tested emission characteristics of pure methyl esters in CI engines and found a decrease in NO_x with saturated C12 and C16 methyl esters relative to diesel fuel, while monounsaturated C18 increased slightly the NO_x emissions. Zhang and Boehman [20] claimed that the double bonds contained in biodiesel leads to formation of free radicals that promotes prompt NO_x.

The unsaturated fatty acid molecules have high bulk modulus or low compressibility which leads to earlier injection fuel and NO_x formation. The presence of double bonds in unsaturated fatty acids causes less linear chains, thus leaving less space for molecules to squeeze closer together and hence reduces compressibility [6]. As mentioned previously, less compressible fuel tend to advance of injection timing and increase in NO_x emissions. Observation made by Ban-Weiss et al. [32] concluded that the double bonded

Table 2
Bulk modulus, density and speed of sound of different biodiesel fuels [70].

Fuel	Bulk modulus at 34.5 MPa			Density at 34.5 MPa			Velocity of sound at 34.5 MPa		
	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
Certified D2 diesel	1995.1	1805.6	1634.5	0.8606	0.8494	0.8366	1522.6	1458.0	1397.8
Methyl yellow grease	2128.3	1929.9	1749.7	0.893	0.8800	0.867	1543.8	1480.9	1420.4
Methyl soy ester	2155.1	1952.5	1775.1	0.9005	0.8879	0.8756	1547.0	1482.9	1423.9
Methyl oxidized soy ester	2160.0	1958.0	1779.3	0.9029	0.8892	0.8769	1547.0	1483.9	1424.5
Methyl hydrogenated soy	–	1914.0	1736.5	–	0.8736	0.8642	–	1480.2	1417.5
Methyl canola ester	2152.1	1951.9	1773.4	0.8986	0.8860	0.872	1547.6	1484.3	1426.0
Methyl lard ester	2122.0	1918.2	1746.6	0.8935	0.8804	0.8679	1541.0	1476.2	1418.5
Methyl tallow ester	2124.7	1911.3	1728.7	0.8900	0.8771	0.8642	1545.1	1476.2	1414.4

molecules of biodiesel tend to have a higher adiabatic flame temperature which results in increase of NO_x. On the contrary, Glaude et al. [79] report that the adiabatic flame temperature of biodiesel is equal to or lower than conventional diesel fuels.

High degree of saturation is not always favourable to NO_x reduction because saturated and lower carbon chain length components tend to increase flame temperature. The saturated components like methyl palmitate and methyl stearate could be associated with a higher tendency to produce NO_x than unsaturated components [80]. Tat et al. [81] tested the engine fuelled with high-oleic (unsaturated) soybean biodiesel and reported that unsaturated biodiesel significantly reduces NO_x. The cetane number of biodiesel can vary widely based on differences in fatty acid composition, chain length and the saturation level. High cetane values (CN) were observed for saturated fatty esters and it increases with chain length [82]. Generally, higher CN of fuels tend to reduce NO_x emissions in CI engines. Recently, Pattamaprom et al. [83] conducted performance and emissions test using palm olein and palm stearin (co-products of palm oil refining processes) biodiesel fuels and found that higher chain length olein produced more NO_x than the short chain length stearin.

The location of double bonds and configurations (cis or trans) also affects the physical properties of biodiesel. Most naturally occurring unsaturated fatty acids are in the cis configuration and can be converted into trans configuration by isomerisation. The physical properties of trans configured unsaturated fatty acids are analogous to those of a fully saturated fatty acids. Hass et al. [84] attempted to reduce biodiesel NO_x effect using reformulated (trans configured) biodiesel and found that isomerised biodiesel have increased NO_x emissions by 2.7%. Moreover, they tested transesterified soy polyols (fatty acids containing hydroxyl group) and found a decrease in NO_x emissions (5.6%).

Reducing the number of double bonds in unsaturated fatty acids has often been proposed to return the NO_x emissions level back to that observed with petrodiesel. The double bonds can be reduced either by hydrogenation or by blending an appropriate amount of saturated methyl ester to the biodiesel. Chapman et al. [85] have tested the blend of caprylic acid methyl ester (C8:0) and capric acid methyl ester (C10:0) with B100 and found a NO_x emission reduction of 2.8% relative to petrodiesel. They also conducted experiments on hydrogenated fatty acid and did not find any reduction in NO_x. Moser et al. [8] examined partially hydrogenated soybean oil methyl esters blend with diesel (B20) and found that the reduction in double bond content of partially hydrogenated soybean oil methyl esters blend did not result in a statistically significant difference in NO_x emissions compared with soybean oil methyl esters. High degree of saturation and longer chain length of fatty acids tends to increase in cloud point which may cause clogging of fuel filters and fuel lines. Several approaches have been proposed to reduce the cloud point of biodiesel including: properties modification of feedstocks; blending with petrodiesel; and the use of additives [86].

4.3. *Effect of fuel-bound oxygen*

Biodiesel is an oxygenated fuel containing 11% of oxygen by weight [87]. High oxygen content of biodiesel promotes combustion efficiency and reduces emissions of CO, PM, HC and other pollutants [88,89]. However, many early studies suggested that high combustion efficiency leads to high reaction temperature and NO_x formation [88,90,91].

Graboski et al. [92] observed 1% increase in NO_x at 2% (by weight) oxygen in the fuel and also found that the increase in NO_x is directly correlated with oxygen levels. Song et al. [93] reported that both the enrichment of intake oxygen and the use of oxygenated fuels increase NO_x emissions. A recent study by Hulwan et al. [94] has shown that addition of oxygenated fuel ethanol with Jatropha methyl ester increased the NO_x emissions significantly. Jacobs and Rathore [95] conducted an experiment to investigate the role of fuel-bound oxygen in biodiesel on increases in NO_x emissions. Based on the results they concluded that the lower oxygen consumption efficiency of biodiesel leads to an increase in availability of oxygen to form NO_x.

The presence of oxygen in the fuel structure of biodiesel exhibits low compressibility. The fuel bound oxygen creates a permanent dipole moment in the molecule which results in stronger hydrogen bonding and increased molecular affinity of oxygenated fuels. This in turn leads to reduction of free space between molecules and decreasing its compressibility, consequently an increase in NO_x [8]. Mccormick et al. [38] reported that the oxygen content of biodiesel molecules cause an increase in boiling point and may reduce the rate of droplet evaporation and a change premixed burn fraction of biodiesel fuel and thus NO_x formation. Similar observation is also reported by Mueller et al. [27]. The fuel bound oxygen of biodiesel affects mixture stoichiometry at the lift-off length that may cause increase in NO_x [96]. On the contrary, Lapuerta et al. [97] argued that the oxygen content of biodiesel could not be the reason for increase in NO_x because the oxygen/fuel mass ratio of biodiesel (2.92) remains below that of the petrodiesel (3.58). Nurun Nabi [98] has also shown that the adiabatic flame temperature and NO_x emissions decrease linearly with the increase in oxygen content. In addition, Yuan et al. [99] found no correlation between oxygen content of fuel and NO_x emissions.

Biodiesel combustion generally produces lesser soot than conventional diesel because of fuel bound oxygen, reduced aromatic content, absence of sulphur, and unsaturated fatty acid contents. The reduced soot formation may lessen radiative heat transfer from soot particles which results in elevated reaction temperature and more NO_x. Jacobs et al. [100] found no linear correlation between biodiesel soot formation and NO_x emissions. Paivi et al. [101] experimented rapeseed and soybean methyl esters using a Volvo bus engine and observed a 40% reduction of soot. The structural oxygen content of fuel could cause lessening of soot formation by effectively removing carbon from reaction pathways that lead to soot precursors [50]. Krahl et al. [102] studied the size of the soot emitted from both biodiesel and diesel and found that biodiesel produced smaller size soot particles than conventional diesel. The presence of surface oxygen on soots leads to surface burning that occurs progressively from the outermost periphery. This may cause diameter reduction of soot particle [103]. The smaller size soot particles produced by biodiesel has more reactive sites for oxidation. The nanostructure of soot provides more surface area for oxidation which results in reduced soot formation [50]. Mueller et al. [31] showed that fuel bound oxygen is more effective at reducing in-cylinder soot than oxygenated additives. McEnally and Pfefferle [104] studied the effect of fuel bound oxygen on soot formation. Results indicated that sooting tendencies of esters depend strongly on molecular structure and increase in the following order: methyl and ethyl esters, carboxylic acids, propyl esters and n-alkanes, and butyl and pentyl esters. Moreover, Egolfopoulos et al. [105] observed more soot emissions from unsaturated biodiesel fuels than saturated ones. To reduce the biodiesel NO_x effect, decreasing fuel bound oxygen content may not be the right strategy because the presence of oxygen not only reduces particulate matter and also mutagenicity of the soot particles [106].

4.4. *Effect of cetane number*

The ignition and combustion quality of diesel and biodiesel of diesel engine fuel is measured with a dimensionless descriptor called cetane number (CN). Higher cetane number fuels tend to increase power output, reduce exhaust smoke, increase cold start

properties, reduce combustion noise and reduce exhaust odour [107]. Too low CN leads to engine misfiring, higher air temperature and incomplete combustion. The high value of CN may also cause operational problems like incomplete combustion and smoke. In general, higher CN is associated with shorter ignition delay, lower average combustion temperatures and decreased residence time, consequently less NO_x formation [4].

Generally, biodiesel fuel has higher cetane number than conventional diesel fuel. Despite the high cetane value, NO_x emissions usually increase with the use of biodiesel. Zheng et al. [108] observed that biodiesel with a CN similar to the diesel produced more NO_x emissions than the diesel and biodiesel with a higher CN had comparable NO_x emissions with the diesel. Data presented in Table 1 also indicate high cetane value biodiesel exhibits low NO_x emissions. In contrast, Wang et al. [109] have suggested that high CN of biodiesel tend to increase peak pressure and temperature due to shortened ignition delay which enhances NO_x formation. Moreover, Knothe [110] found non-linear relationship between the ignition delay period and the CN. A research by McCormick et al. [75] has shown that CN of biodiesel is linearly correlated with saturated fatty acids content and chain length. Furthermore, Knothe et al. [111] studied the influence of compound structure on CN by using ignition quality tester and confirmed that the CN of fuel is increases with saturated fatty acid content. Short chain branched esters have low CN, but they exhibit good cold flow properties [110]. Tat [112] examined the effect of cetane improver 2-ethylhexyl nitrate (EHN) on soybean oil methyl ester (SME) combustion parameters and compared with those of yellow grease methyl ester (YGME). He observed that as the cetane number was increased from 50.4 to 62.6, the ignition delay period and premixed portion of combustions was reduced approximately 10% and 47% respectively. As mentioned above shorted ignition delay period and reduced premixed portion of combustions are responsible for lowered NO_x emissions.

Cetane number of biodiesel can be increased by structural modification of fuel or by addition of cetane improvers with fuel. A review by Hoekman et al. [113] showed that cetane values of the biodiesel increases with chain length and decreases with chain branching and degree of unsaturation. Wadumesthrige et al. [114] have found that atmospheric oxidation of biodiesel enhances CN of fuel due to the formation of hydroperoxides, aldehydes and oligomers of fatty acid methyl esters. Canoira et al. [115] nitrated the biodiesel derived from waste frying oil to enhance the CN by reacting biodiesel with nitric acid and acetyl nitrate and they observed 8.3% increase in CN. McCormick [12] of NREL reported that the addition of cetane improvers DTBP and EHN are effective in reducing biodiesel NO_x emissions.

4.5. Effect of fuel viscosity

Generally, biodiesel would be considered a high viscous fuel than conventional diesel. The higher viscosity causes reduced fuel leakage during injection, which results in increase of pressure and an advance in injection timing [67]. As mentioned above the advance in injection timing leads to an increase of mass injection rate and NO_x. Furthermore, Usta [116] observe the increased injected mass in the case of biodiesel by means of an increase in viscosity. Higher viscosity of fuel also tends to poor atomization, smaller spray cone angles, high spray jet penetration and larger overall average droplet sizes. Smaller spray cone angles and advanced start of injection are the main reasons for increased NO_x emissions of biodiesel. The decreased spray cone angle and increased spray penetration may increase the degree of widespread combustion in the engine combustion chamber, which could increase NO_x emissions [36]. Furthermore, the increased penetration length may cause air and fuel spray mixed more slowly near the spray tip due to slower velocities resulting in more time for NO formation [117]. Deshmukh et al. [118] observed an intact liquid core in biodiesel's spray pattern even at injection pressures as high as 1600 bar. Yuan and Hansen [36] examined the effect of viscosity on NO_x emissions and observed a 3.52% reduction in NO_x emissions when the viscosity of soy methyl ester decreased to a level of D2 diesel. Moreover, Anderson and Olsen [119] analysed NO_x as a function of viscosity and they observed an increase of NO_x with increase in viscosity at low temperatures. However, while preheating the fuel to 75 °C this trend is reversed. Finally, they concluded that vegetable oils that are high in polyunsaturated fatty acids (e.g. linoleic and linolenic acid) are less viscous, but contribute to higher NO_x emissions.

4.6. Effect of fuel density

The density of the fuels affects the start of injection, the injection pressure, and the fuels spray characteristics, so that they influence combustion and emissions. Furthermore, it acts as a precursor for a number of other fuel properties such as heating value and viscosity. Modern diesel engine fuel injection systems measure the fuel by volume. So the changes in the fuel density will influence mass of fuel injected and NO_x [120]. McCormick et al. [75] found a correlation between higher density and iodine value. NREL report [12] suggest that blending with a low density fuels such as aromatic diesel, kerosene, or Fischer–Tropsch diesel is effective at reducing biodiesel NO_x emissions. Moreover, Boehman et al. [121] observed lower NO_x emissions with low density paraffinic fuels. In contrast, Kook and Pickett [122] claimed that the fuel density do not significantly affect the total entrainment and mixing into the spray.

4.7. Effect of surface tension

The higher surface tension and viscosity of fuel offer resistance to atomization during injection process. The surface tension of biodiesel is 22% higher than that of petrodiesel [123]. Ahmed et al. [124] studied the effect of surface tension on peanut, coconut and canola methyl esters and observed smallest mean drop size with coconut methyl ester due to its lowest surface tension value. Table 1 indicates coconut methyl ester emits lowest NO_x when compared to other biodiesel fuels. Moreover, Hansen [36] examined the effect of surface tension and heat of vapourization on NO_x emissions with soy methyl ester (SME) fuel and found that these properties did not contribute to the increased NO_x.

4.8. Effects of thermal properties

Liquid thermal conductivity and vapour heat capacity of fuel affects heat transfer between the drop interior and the surface, temperature distribution of gas mixtures surrounding the spray drops and air fuel ratio. For biodiesel these properties are slightly lower than that of the diesel [125]. The thermal diffusivity of biodiesel vapour is much lower than that for diesel by as much as a factor of 20 [126]. Changes in these properties are expected to have a significant influence on atomization and NO_x formation rate.

5. Summary and conclusions

A systematic review of the published literature on the effect of fuel properties and composition that influence biodiesel NO_x emissions has been carried out and main findings are summarised.

1. The majority of studies have shown that NO_x emissions for biodiesel are significantly increased, compared with diesel.

2. In general, thermal NO is a dominant mechanism in the combustion processes; however, prompt NO also contributes significantly in biodiesel combustion.
3. Several factors are reported to contribute to increased NO_x emissions in biodiesel: advancement of injection timing, increased adiabatic flame temperature, higher heat release rate, more stoichiometric burning, lessened radiative heat transfer from soots, increased premixed burn fraction, decreased spray cone angle and widespread high-temperature distribution areas.
4. Biodiesel combustion is a low temperature reaction and the change in thermal NO_x formation could not be the major reason for biodiesel NO_x effect.
5. The artificial advance in injection timing as a result of biodiesel's higher bulk modulus may result in increased mass delivery and reaction temperature, thus increasing NO_x formation. This effect can be reduced by retarding the injection timing or by preheating the fuel.
6. NO_x emissions are linearly correlated with iodine value of fatty acid ester. Fuel composition has effects on bulk modulus of compressibility, adiabatic flame temperature, degree of saturation and cetane number and changes in these properties may also play a role in NO_x formation.
7. Most authors point to fuel-bound oxygen content of biodiesel as reason for increased NO_x emissions. The presence of oxygen in biodiesel suppresses the formation of soot particle which results in reduced radiative heat transfer, causing increased reaction temperature and thus NO_x.
8. Biodiesel with a higher CN had comparable NO_x emissions with the diesel.
9. The properties that affect atomization characteristics such as viscosity, density, surface tension, liquid thermal conductivity, vapour heat capacity and thermal diffusivity also have a significant influence on NO_x formation.

Further studies will be needed to determine the effect of fuel composition on prompt NO_x formation and the influence of fuel atomization on biodiesel NO_x effect. Furthermore, research on genetic modification of biodiesel feedstock composition that gives lowest NO_x emissions is also needed.

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